(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 604 798 A1**

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 93119754.5

(22) Date of filing: 08.12.93

(51) Int. Cl.5: **A01N 37/28**, A01N 37/52, A01N 43/40, A01N 43/58, C07C 257/22

(30) Priority: 29.12.92 US 998105
29.12.92 US 998104
29.12.92 US 998101

(43) Date of publication of application:
06.07.94 Bulletin 94/27

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IE IT LI LU NL PT SE

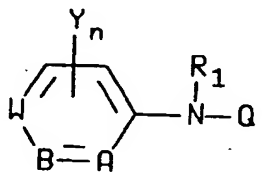
(71) Applicant: AMERICAN CYANAMID COMPANY
One Cyanamid Plaza
Wayne New Jersey 07470(US)

(72) Inventor: Furch, Joseph Augustus
68 Northbrook Avenue
Lawrenceville, New Jersey(US)
Inventor: Kuhn, David George
2 Adrian Place
Newton, Pennsylvania(US)
Inventor: Hunt, David Allen
9 Water Lily Way
Newton, Pennsylvania(US)
Inventor: Lew, Albert Chieh
7 Cambridge Way
Princeton Junction, New Jersey 08850(US)
Inventor: Gronostajski, Cynthia Emma
530 Roebling Avenue
Trenton, New Jersey 08611(US)

(74) Representative: Wächtershäuser, Günter, Dr.
Tal 29
D-80331 München (DE)

(54) **N-arylhydrazine derivatives as insecticidal and acaricidal agents.**

(57) There are provided N-arylhydrazine derivatives of formula I



(I)

the use thereof for the control of insect and acarid pests and methods and compositions for the protection of crops from the damage and loss caused by said pests.

EP 0 604 798 A1

BACKGROUND OF THE INVENTION

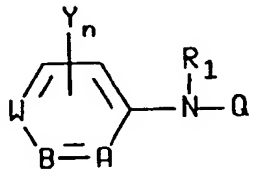
Certain insect and acarid pests are harmful and cause enormous losses annually in agricultural crops, stored products and human and animal health. It is an object of this invention to provide substituted N-arylhydrazine derivatives which are effective agents for the control of pestiferous insects and acarina.

It is another object of this invention to provide a method for the protection of important agronomic crops from the harmful and damaging effects caused by insect and acarid pests.

It is a further object of this invention to provide insecticidal and acaricidal compositions.

SUMMARY OF THE INVENTION

The present invention provides a method for the control of insects or acarina which comprises contacting said insects or acarina or their food supply, breeding ground or habitat with an insecticidally effective amount of an N-arylhydrazine derivative of formula I



(I)

wherein

A is C-R_4 or N;

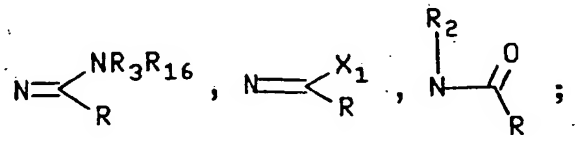
B is C-R_5 or N;

W is C-R_6 or N with the proviso that one of A, B or W must be other than N;

Y is hydrogen, halogen, CN, NO_2, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy or C_1-C_6haloalkoxy;

n is an integer of 0, 1 or 2;

Q is



R is hydrogen, C_1-C_{10}alkyl optionally substituted with one or more halogens, C_3-C_6 cycloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,(C_1-C_4alkyl)SO_x, (C_1-C_4haloalkyl)SO_x, phenyl optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,(C_1-C_4alkyl)SO_x, (C_1-C_4haloalkyl)SO_x, NO_2 or CN groups, or

phenoxy optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, (C_1-C_4alkyl)SO_x, (C_1-C_4haloalkyl)-SO_x, NO_2 or CN groups,

C_3-C_{12} cycloalkyl optionally substituted with one or more halogens, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, (C_1-C_4alkyl)SO_x, (C_1-C_4haloalkyl)SO_x, phenyl optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, NO_2 or CN groups, or phenoxy optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, NO_2 or CN groups, or

phenyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, NO_2 or CN groups;

R_1 and R_2 are each independently hydrogen or C_1-C_4alkyl;

R_3 and R_{16} are each independently hydrogen,

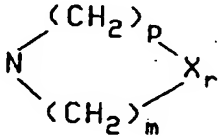
C_1-C_{10}alkyl optionally substituted with one or more halogen, hydroxy, C_1-C_4alkoxy, (C_1-C_4alkyl)SO_x, $CONR_7R_8$, CO_2R_9, R_{10}, R_{11}, C_3-C_6cycloalkyl optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, NO_2 or CN groups,
phenyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, CO_2 or CN groups, or pyridyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, NO_2 or CN groups,

C_3-C_{10}alkenyl optionally substituted with one or more halogen, hydroxy, C_1-C_4alkoxy, (C_1-C_4alkyl)SO_x, $CONR_7R_8$, CO_2R_9, R_{10}, R_{11}, C_3-C_6cycloalkyl optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,NO_2 or CN groups,
phenyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, CO_2 or CN groups, or pyridyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, NO_2 or CN groups,

C_3-C_{10}alkynyl optionally substituted with one or more halogen, hydroxy, C_1-C_4alkoxy, (C_1-C_4alkyl)SO_x, $CONR_7R_8$, CO_2R_9, R_{10}, R_{11}, C_3-C_6cycloalkyl optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,NO_2 or CN groups,
phenyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, CO_2 or CN groups, or pyridyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, NO_2 or CN groups,

C_3-C_{12}cycloalkyl optionally substituted with one or more halogen, hydroxy, C_1-C_4alkoxy, (C_1-C_4alkyl)SO_x, $CONR_7R_8$, CO_2R_9, R_{10}, R_{11}, C_3-C_6cycloalkyl optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, NO_2 or CN groups, phenyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, CO_2 or CN groups, or pyridyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, NO_2 or CN groups or

R_3 and R_{16} may be taken together to form a ring represented by the structure

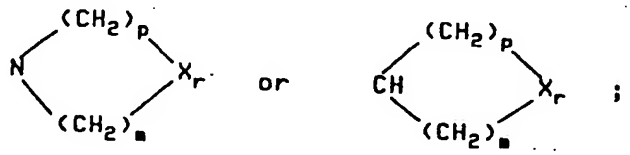


;

R_4, R_5 and R_6 are each independently hydrogen, halogen, CN, NO_2, (C_1-C_4alkyl)SO_x, (C_1-C_4haloalkyl)SO_x, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_6alkoxy or C_1-C_6haloalkoxy;

R_7, R_8 and R_9 are each independently hydrogen or C_1-C_4 alkyl;

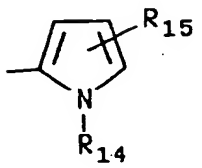
R_{10} is $NR_{12}R_{13}$,



or

;

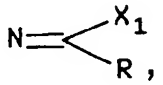
R_{11} is



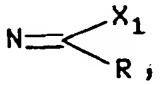
;

R_{12}, R_{13}, R_{14} and R_{15}	are each independently hydrogen or C_1-C_4 alkyl;
X_1	is chlorine, bromine, or fluorine;
X	is O, S or NR_{14};
r	is an integer of 0 or 1;
p and m	are each independently an integer of 0, 1, 2 or 3 with the provisos that only one of p, m or r can be 0 and that the sum of p + m + r must be 4, 5 or 6;
x	is an integer of 0, 1 or 2; or

the acid addition salts thereof, with the proviso that when Q is

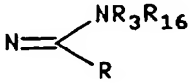


R is C_1-C_5 alkyl and X_1 is chlorine, then either at least one of A, B or W must be N or R_4, R_5, R_6 and Y must be other than hydrogen and n must be O and with the further proviso that when Q is



R is phenyl or substituted phenyl and X_1 chlorine, then at least one of A, B or W must be N.

The present invention further provides N-arylamidrazone compounds of formula I wherein A, B, W, Y, n, and R_1, are as described hereinabove and Q is



with the proviso that when all of A, B and W are other than N, then R and one of R_3 or R_{16} must be other than hydrogen and with the further proviso that when one of A, B or W is N, then Y, R_4, R_5 or R_6 must be other than C_1-C_{10} alkyl.

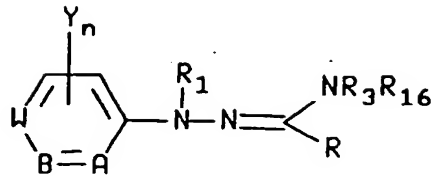
Compositions and methods for the protection of growing plants from attack and infestation by insects and acarina are also provided.

DETAILED DESCRIPTION OF THE INVENTION

A variety of insects and acarina cause great economic loss by damaging or destroying agricultural crops and other valuable plants; by aiding in the spread and development of bacteria, fungi and viruses that produce diseases of plants; and by destroying or lowering the value of stored foods, other products and possessions. Insects and acarina present some of the farmers' greatest problems the world over. The need for alternative and effective insect and acarid control is a global concern.

It has now been found that the substituted N-arylhydrazone derivatives of formula I are especially efficacious insecticidal and acaricidal agents, particularly against Coleoptera, Lepidoptera and Acarina.

The formula Ia amidrazone compounds of the present invention have the structural formula

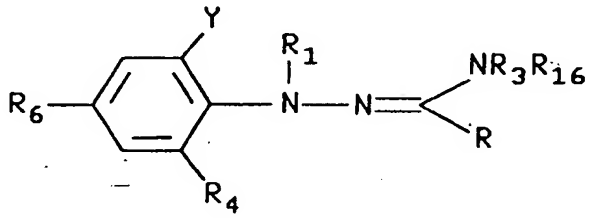


(Ia)

wherein A, B, W, Y, n, R, R_1, R_3 and R_{16} are described hereinabove. The term halogen as used in the specification and claims designates chlorine, fluorine, bromine or iodine. The term acid addition salts designates those salts formed by acids commonly known in the art such as hydrogen chloride, hydrogen bromide, hydrogen bisulfate, hemi-hydrogen sulfate and the like. In the above definition when n is O then Y is hydrogen.

Preferred compounds of the invention are those wherein R, R_3 and R_{16} are each independently hydrogen or C_1-C_6alkyl, A is C-R_4, B is C-R_5, W is C-R_6, Y is halogen and n is 1. Particularly preferred compounds are those wherein R_1 is hydrogen, R_4 is halogen, R_5 is hydrogen and/or R_6 is C_1-C_6alkyl substituted with one or more halogens, preferably trifluoromethyl.

Other preferred compounds of the invention are compounds having the structure

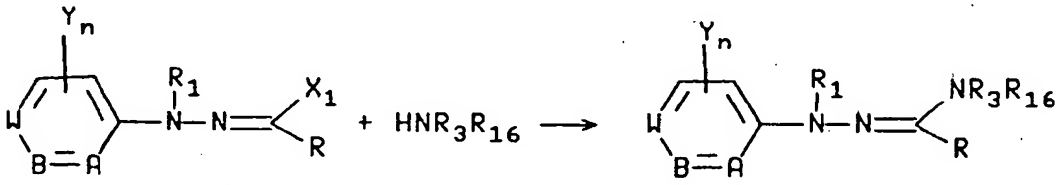


wherein

R	is C_1-C_{10}alkyl;
R_1	is hydrogen or C_1-C_4alkyl;
R_3	is C_1-C_{10}alkyl;
R_{16}	is hydrogen or C_1-C_{10}alkyl; and
R_4, R_6 and Y	are each independently hydrogen, halogen, CN, NO_2, C_1-C_6alkyl, C_1-C_6 haloalkyl, C_1-C_6 alkoxy, or C_1-C_6 haloalkoxy.

The N-arylamidrazones of formula Ia may be prepared by reacting an acid chloride, hydrazone (hydrazinoyl chloride) of formula II with an amine compound, HNR_3R_{16}, as shown in flow diagram I.

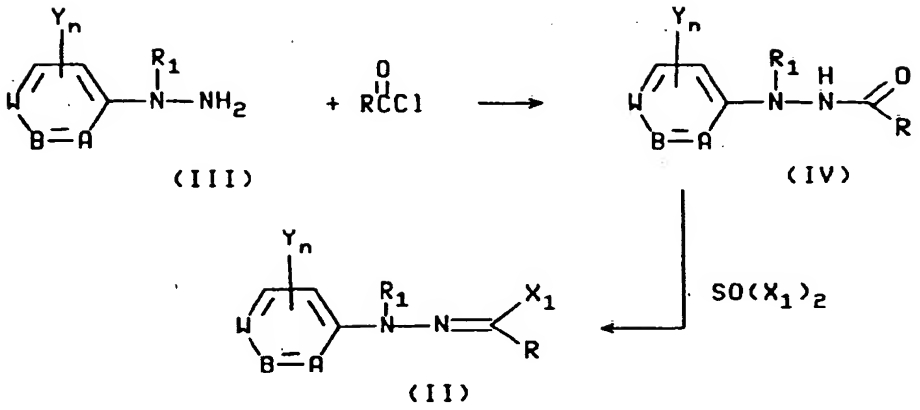
Flow Diagram I



(II) (Ia)

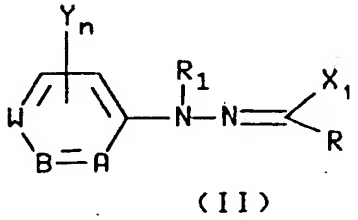
Compounds of formula II may be prepared by reacting a suitable arylhydrazine of formula III with the appropriate acid chloride, RCOCl, to obtain an N-arylhydrazide of formula IV and reacting the formula IV hydrazide with a halogenating agent such as thionyl halide to give the desired formula II N-arylhydrazinoyl halide product. The reaction is illustrated in flow diagram II.

Flow Diagram II



The substituted N-arylhydrazine derivatives of the present invention are effective for controlling insect and acarid pests. Said compounds are also effective for protecting growing or harvested crops from attack and infestation by such pests.

Compounds useful in the inventive method include N-arylhydrazinoyl halide compounds of formula II. The insecticidal and acaricidal formula II hydrazinoyl halides of the present invention have the structural formula



wherein A, B, W, Y, n, R, R_1 and X_1 are described hereinabove.

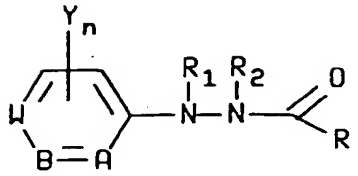
Preferred compounds of formula II are those compounds wherein R_1 is hydrogen, A is C-R_4, B is C-R_5, W is C-R_6, Y is halogen or nitro and n is 1. Particularly preferred are those wherein R_4 is halogen, R_5 is hydrogen and R_6 is C_1-C_6 alkyl substituted with one or more halogens, preferably trifluoromethyl.

Other preferred compounds of formula II are those in which R is optionally substituted C_3-C_{12} cycloalkyl or C_1-C_{10} haloalkyl, preferably C_1-C_6 haloalkyl.

Compounds of formula II wherein X_1 is fluorine may be prepared from compounds of formula II wherein X_1 is chlorine or bromine by a halogen exchange reaction using sodium fluoride or hydrogen fluoride such as that described by March in Advanced Organic Chemistry, 4 Ed. (1992), p. 438.

Further compounds useful in the method of invention include substituted carboxylic acid, N-aryl-hydrazide compounds of formula V.

The insecticidal and acaricidal formula V N-arylhydrazides of the present invention have the structural formula

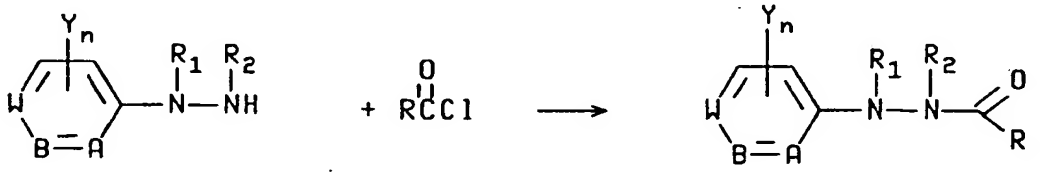


(V)

Preferred compounds of formula V for use in the method of the invention are those compounds wherein R is hydrogen or C_1-C_6alkyl, A is C-R_4, B is C-R_5, W is C-R_6, Y is halogen or nitro and n is 1. Particularly preferred formula V N-arylhydrazides are those wherein R_4 is halogen, R_5 is hydrogen and R_6 is C_1-C_6alkyl substituted with one or more halogens, preferably trifluoromethyl.

Compounds of formula V may be prepared by reacting a suitable arylhydrazine of formula VI with the appropriate acid chloride, RCOCl, to yield the desired N-arylhydrazide of formula V. The reaction is illustrated in flow diagram III.

Flow Diagram III



(VI) (V)

Growing or harvested crops may be protected from attack or infestation by insect or acarid pests by applying to the foliage of the crops, or to the soil or water in which they are growing, a pesticidally effective amount of a formula I N-arylhydrazine derivative.

In practice, generally about 10 ppm to 10,000 ppm, preferably about 100 to 5,000 ppm of the formula I compound dispersed in a liquid carrier, when applied to the plants or the soil or water in which they are growing, is effective to protect the plants from insect and acarina attack and infestation. Soil application of the formula I compounds is particularly effective for the control of the post-embryonic development stages of Coleoptera and Diptera. Applications, such as spray applications, of compositions of the invention are generally effective at rates which provide about 0.125 kg/ha to about 250 kg/ha, preferably about 10 kg/ha to 100 kg/ha. Of course, it is contemplated that higher or lower rates of application of the N-arylhydrazine derivatives may be used dependent upon the prevailing environmental circumstances such as population density, degree of infestation, stage of plant growth, soil conditions, weather conditions and the like.

Advantageously, the formula I compounds may be used in conjunction with, or in combination with other biological and chemical control agents including other insecticides, nematicides, acaricides, molluscicides, fungicides and bactericides such as nuclear polyhedrosis viruses, pyrroles, arylpyrroles, halobenzoylureas, pyrethroids, carbamates, phosphates, and the like.

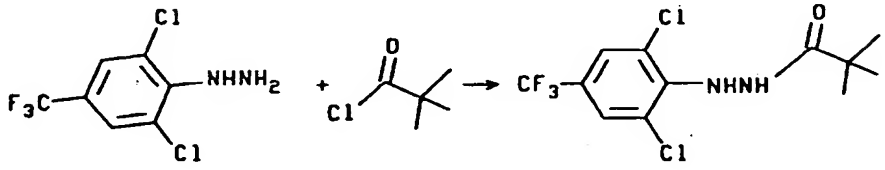
Typical formulations suitable for the formula I N-arylhydrazine derivatives are granular compositions, flowable compositions, wettable powders, dusts, microemulsions, emulsifiable concentrates and the like. All compositions which lend themselves to soil, water and foliage application and provide effective plant protection are suitable. Compositions of the invention include the formula I N-arylhydrazine derivatives admixed with an inert solid or liquid carrier.

Where compositions of the invention are to be employed in combination treatments with other biological or chemical agents, the composition may be applied as an admixture of the components or may be applied sequentially.

For a more clear understanding of the invention, specific examples thereof are set forth below. These examples are merely illustrative, and are not to be understood as limiting the scope and underlying principles of the invention in any way.

EXAMPLE 1

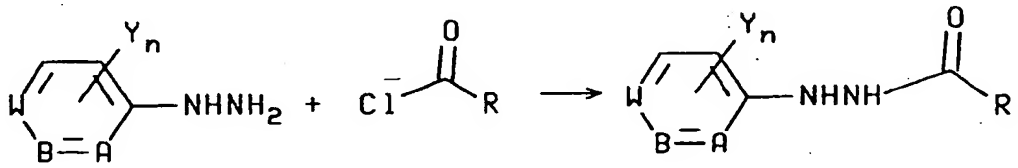
Preparation of 2,2-Dimethylpropionic acid,2-(2,6-dichloro-α,α,α-trifluoro-p-tolyl)hydrazid



A solution of 2,6-dichloro-4-(trifluoromethyl)phenylhydrazine (50.0 g, 0.20 mol) in methylene chloride is treated dropwise with trimethylacetyl chloride (30.6 g, 0.254 mol), stirred for 30 minutes, treated with 10% aqueous NaOH and stirred for 3 hours. The phases are separated; the organic phase is washed with water, dried over $MgSO_4$ and concentrated in vacuo to give an off-white solid residue. The solid is recrystallized from 1,2-dichloroethane to give the title product as a white solid, 55 g (82% yield), mp 140-141°, identified by ^{1}HNMR, ^{13}CNMR and IR spectral analyses.

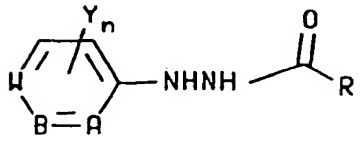
EXAMPLES 2-42

Preparation of substituted N-arylhydrazide derivatives



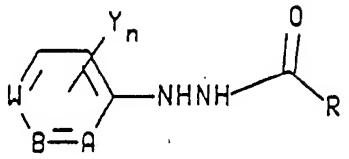
Using essentially the same procedure described above for Example 1 and substituting the appropriate arylhydrazine and acid chloride, the compounds shown in Table I are prepared and identified by ^{1}HNMR, ^{13}NMR and IR spectral analyses.

TABLE I



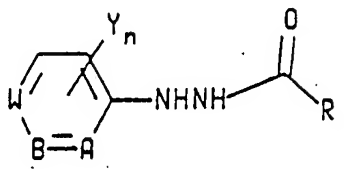
Example Number	A	B	W	Yn	R	mp °C
2	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_2CHCH_2$	135-136
3	C-Cl	CH	C-Cl	6-Cl	$(CH_3)_3C$	124-125.5
4	C-Cl	CH	CH	6-Cl	$(CH_3)_3C$	114-115
5	C-Br	CH	C-CF_3	6-Br	$(CH_3)_3C$	118-120
6	C-Br	CH	C-CF_3	6-Br	CH_3	173-175
7	C-Br	CH	C-CF_3	6-Br	C_6H_5	181-184

TABLE I (Continued)



Example Number	A	B	W	Yn	R	mp °C
8	C-CH_3	CH	C-Cl	H	$(CH_3)_3C$	103-106
9	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3CCH_2$	125-127
10	C-Cl	CH	C-Cl	6-Cl	pClC_6H_5	188-190
11	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_2CH$	158-159
12	C-Cl	CH	C-Cl	6-Cl	cyclopropyl	186-188
13	C-Cl	CH	C-CF_3	6-Cl	$CH_3CH_2C(CH_3)_2$	121-123
14	C-H	CH	C-CF_3	H	$(CH_3)_3C$	136-139
15	C-Cl	CH	C-CF_3	H	$(CH_3)_3C$	143-145

TABLE I (Continued)



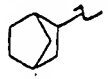
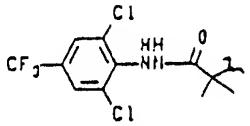
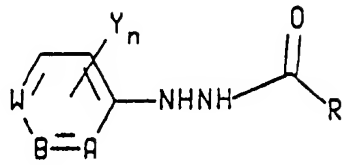
Example Number	A	B	W	Yn	R	mp °C
16	C-Cl	CH	C-CF_3	6-Cl		125-127
17	C-Cl	C-Cl	C-Cl	5,6-diCl	$(CH_3)_3C$	
18	N	CH	C-CF_3	6-Cl	$(CH_3)_3C$	151-151.5
19	C-Cl	CH	C-Cl	6-Cl		138-140
20	C-Cl	CH	C-CF_3	6-Cl	p$ClC_6H_5OC(CH_3)_2$	137-139
21	C-CF_3	CH	CH	H	$(CH_3)_3C$	98-100
22	C-Cl	CH	C-CF_3	6-Cl		101-103
23	C-Cl	CH	C-Cl	6-Cl	cyclohexyl	188-189

TABLE I (Continued)



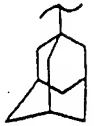
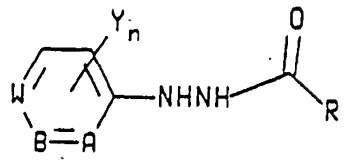
Example Number	A	B	W	Yn	R	mp °C
24	C-Cl	CH	C-CF_3	6-Cl	$C_6H_5C(CH_3)_2$	104-105
25	C-Cl	CH	C-Cl	6-Cl	CF_3CF_2	131-132
26	C-Cl	CH	C-Cl	6-Cl	$(CH_3)_2CH$	164-165
27	C-Cl	CH	C-CF_3	6-Cl	cyclopropyl	172-174
28	C-Cl	CH	C-Cl	6-Cl	$CH_3CH_2C(CH_3)_2$	132-134
29	C-Cl	CH	C-CF_3	6-Cl		160-162
30	C-Br	CH	C-CF_3	6-Br	$(CH_3)_3C$	140-141
31	C-Cl	CH	C-Cl	6-Cl	$CH_3(CH_2)_5C(CH_3)_2$	

TABLE I (Continued)



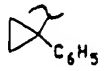
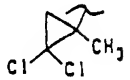
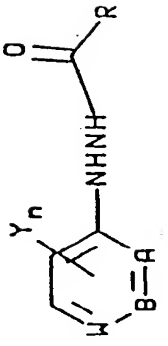
Example Number	A	B	W	Yn	R	mp °C
32	N	N	C-Cl	H	$(CH_3)_3C$	178-182
33	C-Cl	CH	$C-CF_3$	6-Cl		121-123
34	C-Cl	CH	$C-CF_3$	6-Cl	$pClC_6H_5C(CH_3)_2$	105-107
35	C-Cl	CH	$C-CF_3$	6-Cl	$ClCH_2C(CH_3)_2$	119-120
36	C-Cl	CH	$C-CF_3$	6-Cl		174-175
37	C-Cl	CH	C-Cl	6-Cl	$ClCH_2C(CH_3)_2$	124-125
38	C-Cl	CH	CH	$5-CF_3$	$(CH_3)_3C$	170-177.5
39	C-Cl	CH	$C-CF_3$	6-Cl	1-methylcyclohexyl	105-107

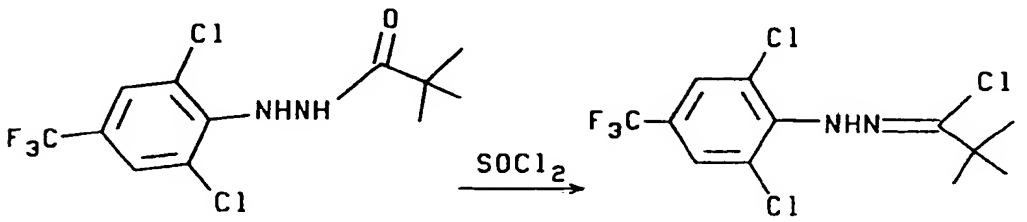
TABLE I (Continued)



Example Number	A	B	W	Yn	R	mp °C
40	CH	C-CF_3	CH	H	$(CH_3)_3C$	158-160
41	C-F	C-F	C-F	5,6-diF	$(CH_3)_3C$	154-157
42	C-Br	CH	F	6-Br	$(CH_3)_3C$	118-120

EXAMPLE 43

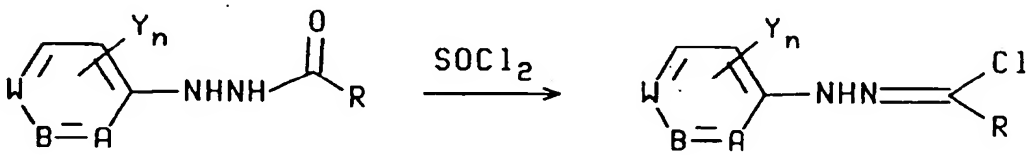
Preparation of 1-chloro-2,2-dimethylpropionaldehyde, 2-(2,6-Dichloro-α,α,α-trifluoro-p-tolyl)hydrazone



A mixture of 2,2-dimethyl-2-(2,6-dichloro-α,α,α-trifluoro-p-tolyl)hydrazide propionic acid (50.0 g, 0.152 mol) and thionyl chloride (53.8 g, 0.452 mol) in toluene is heated at reflux temperature for 8 hours, cooled to room temperature and concentrated in vacuo to give an oil residue. The oil is dissolved in hexanes and passed through a silica gel filtercake. The filtercake is washed with several portions of hexanes. The filtrates are combined and concentrated in vacuo to give the title product as a yellow oil, 47.2 g (90% yield), identified by ^{1}HNMR, ^{13}CNMR and IR spectral analyses.

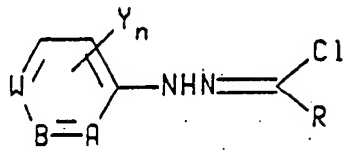
EXAMPLES 44-84

Preparation of substituted N-arylhydrazinoyl chlorides



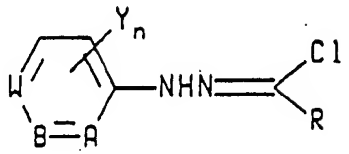
Using essentially the same procedure as described above in Example 43 and substituting the appropriate hydrazide substrate, the compounds shown in Table II are prepared and identified by ^{1}HMR, ^{13}CNMR and IR spectral analyses.

TABLE II



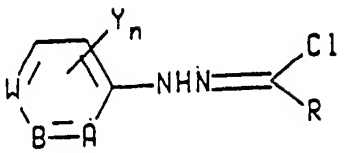
Example Number	A	B	W	Yn	R	mp °C
44	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_2CHCH_2$	
45	C-Cl	CH	C-Cl	6-Cl	$(CH_3)_3C$	44.5-45.5
46	C-Cl	CH	CH	6-Cl	$(CH_3)_3C$	
47	C-Br	CH	C-F	6-Br	$(CH_3)_3C$	
48	C-Br	CH	C-CF_3	6-Br	CH_3	
49	C-Br	CH	C-CF_3	6-Br	C_6H_5	

TABLE II (Continued)



Example Number	A	B	W	Yn	R	mp °C
50	C-CH_3	CH	C-Cl	H	$(CH_3)_3C$	
51	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3CCH_2$	
52	C-Cl	CH	C-Cl	6-Cl	pClC_6H_5	120
53	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_2CH$	
54	C-Cl	CH	C-Cl	6-Cl	cyclopropyl	
55	C-Cl	CH	C-CF_3	6-Cl	$CH_3CH_2C(CH_3)_2$	
56	C-H	CH	C-CF_3	H	$(CH_3)_3C$	

TABLE II (Continued)



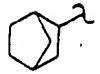
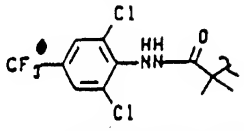
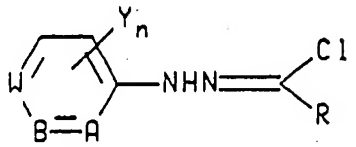
Example Number	A	B	W	Yn	R	mp °C
57	C-Cl	CH	C-CF_3	H	$(CH_3)_3C$	
58	C-Cl	CH	C-CF_3	6-Cl		
59	C-Cl	C-Cl	C-Cl	5,6-diCl	$(CH_3)_3C$	
60	N	CH	C-CF_3	6-Cl	$(CH_3)_3C$	
61	C-Cl	CH	C-Cl	6-Cl		
62	C-Cl	CH	C-CF_3	6-Cl	p$ClC_6H_5OC(CH_3)_2$	
63	C-CF_3	CH	CH	H	$(CH_3)_3C$	

TABLE II (Continued)



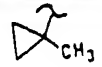
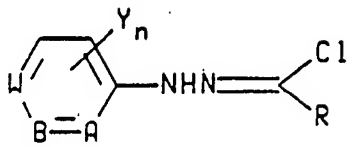
Example Number	A	B	W	Yn	R	mp °C
64	C-Cl	CH	C-CF_3	6-Cl		
65	C-Cl	C-CH	C-Cl	6-Cl	cyclohexyl	
66	C-Cl	C-CH	C-CF_3	6-Cl	$C_6H_5C(CH_3)_2$	
67	C-Cl	CH	C-Cl	6-Cl	CF_3CF_2	
68	C-Cl	CH	C-Cl	6-Cl	$(CH_3)_2CH$	
69	C-Cl	CH	C-CF_3	6-Cl	cyclopropyl	
70	C-Cl	CH	C-Cl	6-Cl	$CH_3CH_2C(CH_3)_2$	

TABLE II (Continued)



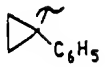
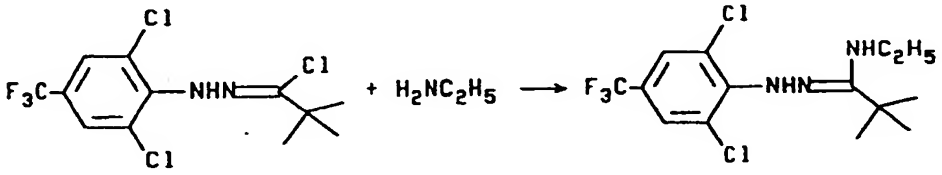
Example Number	A	B	W	Yn	R	mp °C
71	C-Cl	CH	C-CF_3	6-Cl		110-111
72	C-Br	CH	C-CF_3	6-Br	$(CH_3)_3C$	
73	C-Cl	CH	C-Cl	6-Cl	$CH_3(CH_2)_5C(CH_3)_2$	
74	N	N	C-Cl	H	$(CH_3)_3C$	
75	C-Cl	CH	C-CF_3	6-Cl		
76	C-Cl	CH	C-CF_3	6-Cl	p$ClC_6H_5C(CH_3)_2$	85-88
77	C-Cl	CH	C-CF_3	6-Cl	$ClCH_2C(CH_3)_2$	

TABLE II (Continued)

Example Number	A	B	W	Yn	R	mp °C
78	C-Cl	CH	CCF_3	6-Cl		71-73
79	C-Cl	CH	C-Cl	6-Cl	$ClCH_2C(CH_3)_2$	
80	C-Cl	CH	CH	$5-CF_3$	$(CH_3)_3C$	
81	C-Cl	CH	$C-CF_3$	6-Cl	1-methylcyclohexyl	
82	CH	$C-CF_3$	CH	H	$(CH_3)_3C$	
83	CH	CH	CH	5-F	$(CH_3)_3C$	
84	C-Br	CH	F	6-Br	$(CH_3)_3C$	

EXAMPLE 85

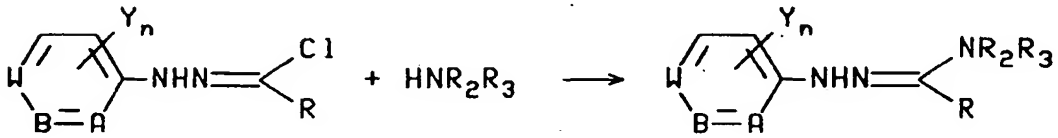
Preparation of N-Ethyl-2,2-dimethylpropionamide, 2-(2,6-Dichloro-α,α,α-trifluoro-p-tolylhydrazone



A solution of (2,6-dichloro-α,α,α-trifluoro-p-tolyl)hydrazone 1-chloro-2,2-dimethylpropionaldehyde (20.0 g, 0.0575 mol) in tetrahydrofuran is treated dropwise with 70% aqueous ethylamine (28.0 g, 0.144 mol) at room temperature, stirred for 1 hour and concentrated in vacuo to give a semi-solid residue. The semi-solid is dispersed in ether and water. The phases are separated; the organic phase is washed with water, dried over $MgSO_4$ and concentrated in vacuo to give the title product as a yellow oil, 19.8 g (97% yield), identified by ^{1}HNMR, ^{13}CNMR and IR spectral analyses.

EXAMPLES 86-169

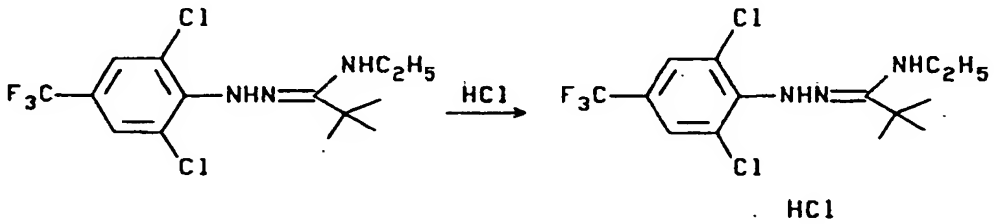
Preparation of substituted N-arylamidrazones



Using essentially the same procedure described above in Example 85 and substituting the appropriate hydrazinoylchloride and a suitable amine, the compounds shown in Table III are prepared and identified by ^{1}HNMR, ^{13}CNMR and IR spectral analyses.

Hydrochloride salts of the invention may be prepared in accordance with the procedure outlined below.

Example 146 - Preparation of N-Ethyl-2,2-dimethylproprionamide,2-(2,6-dichloro-α,α,α-trifluoro-p-tolyl-hydrazone hydrochloride

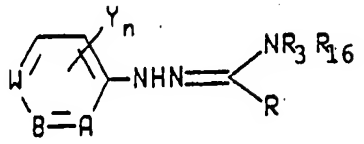


A stirred mixture of N-ethyl-2,2-dimethylpropionamide, 2-(2,6-dichloro-α,α,α-trifluoro-p-tolylhydrazone (0.1 g, 2.8 mmol) and hexane is bubbled through with HCl gas for a 30 minute period. The resultant reaction mixture is filtered to give the title compound as a white solid, 1.13 g, mp 202-202.5°C.

TABLE III

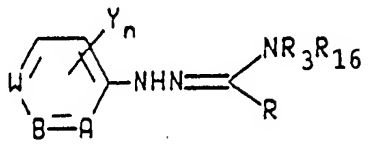
Example Number	A	B	W	Yn	R	R3	R16	mp °C
86	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	pClC_6H_5	H	
87	C-Cl	CH	C-Cl	6-Cl	$(CH_3)_3C$	$CH_3CH_2CH_2$	H	
88	C-Cl	CH	C-Cl	6-Cl	$(CH_3)_2CH$	$CH_3CH_2CH_2$	H	48-50
89	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3CCH_2$	$CH_3CH_2CH_2$	H	
90	C-Cl	CH	C-Cl	6-Cl	$(CH_3)_2CH$	cyclopropyl	H	
91	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3CCH_2$	CH_3CH_2	H	

TABLE III (Continued)



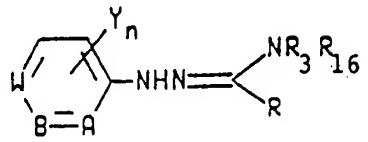
Example Number	A	B	W	Yn	R	R_3	R_{16}	mp °C
92	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_2CH$	CH_3CH_2	H	62-64
93	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	CF_3CH_2	H	
94	C-Br	CH	C-CF_3	6-Br	$(CH_3)_3C$	CH_3CH_2	H	
95	C-Br	CH	C-CF_3	6-Br	$(CH_3)_3C$	$CH_3CH_2CH_2$	H	
96	C-Br	CH	C-CF_3	6-Br	$(CH_3)_3C$	$C_6H_5CH_2$	H	
97	C-Br	CH	C-CF_3	6-Br	$(CH_3)_3C$	furfuryl	H	

TABLE III (Continued)



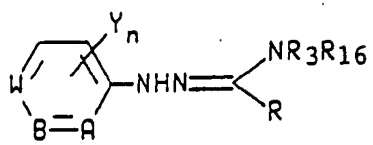
Example Number	A	B	W	Yn	R	R3	R16	mp °C
98	C-Br	CH	C-CF_3	6-Br	CH_3	CH_3CH_2	H	
99	C-Br	CH	C-CF_3	6-Br	C_6H_5	CH_3CH_2	H	
100	C-Cl	CH	C-Cl	6-Cl	$(CH_3)_3C$	H	H	131-135
101	C-Cl	CH	C-Cl	6-Cl	$(CH_3)_3C$	CH_3	CH_3	61-63
102	C-Cl	CH	C-Cl	6-Cl	$(CH_3)_3C$	CH_3CH_2	H	
103	C-Cl	CH	C-CF_3	H	$(CH_3)_3C$	$CH_3CH_2CH_2$	H	
104	C-Cl	CH	CH	6-Cl	$(CH_3)_3C$	$CH_3CH_2CH_2$	H	
105	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	H	H	100-102.5

TABLE III (Continued)



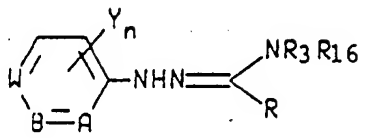
Example Number	A	B	W	Yn	R	R3	R16	mp °C
106	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	CH_3	H	78-79.5
107	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	CH_3	CH_3	
108	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$CH_3CH_2CH_2$	H	
109	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$(CH_3)_3C$	H	67.5-68.5
110	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$(CH_3)_2CHCH_2$	H	
111	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$-CH_2CH_2CH_2CH_2-$		
112	C-Cl	CH	C-Cl	6-Cl	cyclopropyl	CH_3CH_2	H	65-67

TABLE III (Continued)



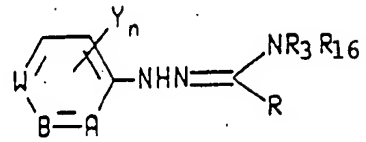
Example Number	A	B	W	Yn	R	R3	R16	mp °C
113	C-Cl	CH	C-CF_3	6-Cl	$CH_3CH_2C(CH_3)_2$	CH_3CH_2	H	
114	C-Br	CH	C-CF_3	6-Br	$(CH_3)_3C$	$(CH_3)_2CH$	H	
115	C-Cl	CH	C-CF_3	H	$(CH_3)_3C$	$-CH_2CH_2CH_2CH_2-$		
116	C-Cl	CH	C-CF_3	6-Cl	$CH_3CH_2C(CH_3)_2$	CH_3CH_2	CH_3CH_2	
117	C-Cl	CH	C-CF_3	H	$(CH_3)_3C$	CH_3CH_2	H	
118	C-Cl	CH	C-Cl	6-Cl	$CH_3CH_2C(CH_3)_2$	CH_3CH_2	H	

TABLE III (Continued)



Example Number	A	B	W	Yn	R	R3	R16	mp °C
119	C-Cl	CH	C-CF_3	6-Cl	$C_6H_5C(CH_3)_2$	CH_3CH_2	H	
120	C-Cl	CH	C-CF_3	H	$(CH_3)_3C$	$-CH_2CH_2CH_2CH_2CH_2-$		
121	CH	CH	C-CF_3	H	$(CH_3)_3C$	CH_3CH_2	H	
122	CH	CH	C-CF_3	6-Cl	$(CH_3)_2CHCH_2$	CH_3CH_2	H	86.5-88.5
123	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$-CH_2CH_2CH_2CH_2CH_2-$		
124	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	cyclohexyl	H	
125	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$C_6H_5CH_2CH_2$	H	

TABLE III (Continued)



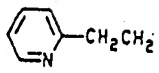
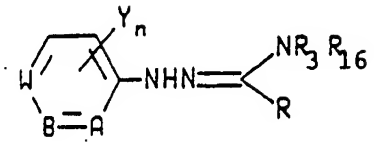
Example Number	A	B	W	Yn	R	R_3	R_{16}	mp °C
126	C-Br	CH	C-F	6-Br	$(CH_3)_3C$	CH_3CH_2	H	
127	C-Cl	C-Cl	C-Cl	5,6-diCl	$(CH_3)_3C$	CH_3CH_2	H	63-65
128	C-Cl	CH	C-Cl	6-Cl	$CH_3(CH_2)_5C(CH_3)_2$	CH_3CH_2	H	
129	C-Cl	CH	C-CF_3	6-Cl		CH_3CH_2	H	
130	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$CH_3(CH_2)_2CH_2$	H	
131	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$(CH_3)_2CH$	H	
132	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$		H	

TABLE III (Continued)



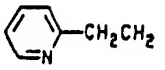
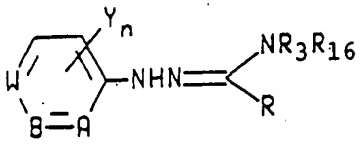
Example Number	A	B	W	Yn	R	R 3	R16	mp °C
133	C-Cl	CH	C-Cl	6-Cl	$pClC_6H_5$	$(CH_3)_2CH$	H	124-127
134	C-Cl	CH	C-Cl	6-Cl	$pClC_6H_5$	CH_3CH_2	H	127-132
135	C-Cl	CH	$C-CF_3$	6-Cl	$C_6H_5C(CH_3)_2$	$C_6H_5CH_2CH_2$	H	
136	C-Cl	CH	$C-CF_3$	6-Cl		CH_3CH_2	H	74-75
137	$C-CF_3$	CH	CH	H	$(CH_3)_3C$	CH_3CH_2	H	
138	C-Cl	CH	$C-CF_3$	H	$(CH_3)_3C$	$C_6H_5CH_2CH_2$	H	
139	C-Cl	CH	$C-CF_3$	H	$(CH_3)_3C$		H	

TABLE III (Continued)



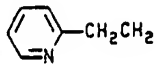
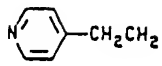
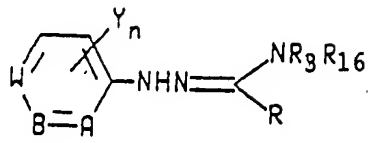
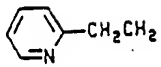
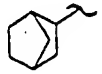
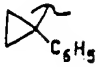
Example Number	A	B	W	Yn	R	R3	R16	mp °C
140	CH	CH	C-CF_3	H	$(CH_3)_3C$		H	
141	C-Cl	CH	C-CF_3	6-Cl	$pClC_6H_5C(CH_3)_2$	CH_3CH_2	H	
142	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$C_6H_5CH(CH_3)$	H	
143	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$(CH_3)_2NCH_2CH_2$	H	
144	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$CH_3CH_2C(CH_3)_2$	H	
145	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$		H	100.5-101.5

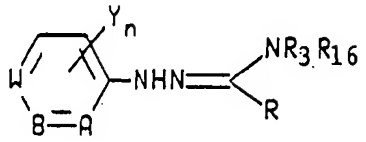
TABLE III (Continued)



Example Number	A	B	W	Yn	R	R3	R16	mp °C
146*	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	CH_3CH_2	H	202-202.5
147	C-Br	CH	C-CF_3	6-Br	$(CH_3)_3C$		H	
148	C-Cl	CH	C-CF_3	6-Cl		CH_3CH_2	H	
149	C-Cl	CH	C-CF_3	6-Cl		CH_3CH_2	H	
150	C-Cl	CH	C-CF_3	6-Cl	$CH_3CH_2C(CH_3)_2$	$C_6H_5CH_2CH_2$	H	
151	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$C_6H_5CH_2$	H	

*Hydrochloride salt

TABLE III (Continued)



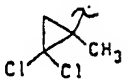
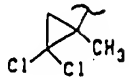
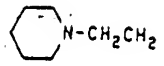
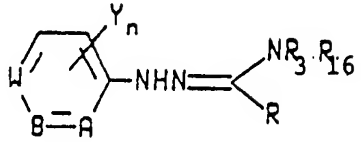
Example Number	A	B	W	Yn	R	R3	R16	mp °C
152	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	CH_3CH_2	CH_3CH_2	
153	C-Cl	CH	C-CF_3	6-Cl		CH_3CH_2	H	
154	C-Cl	CH	C-CF_3	6-Cl		$(CH_3)_2CH$	H	
155	C-Cl	CH	C-CF_3	6-Cl	$ClCH_2C(CH_3)_2$	p$CF_3OC_6H_5$	H	203-205
156	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	neopentyl	H	
157	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$H_2NCOCH(CH_3)_2$	H	160-162
158	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$		H	
159	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	pClC_6H_5-CH_2CH_2	H	

TABLE III (Continued)



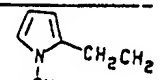
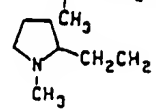
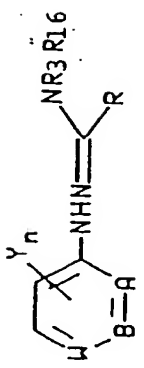
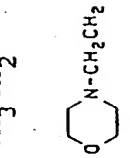
Example Number	A	B	W	Yn	R	R3	R16	mp °C
160	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$		H	
161	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$		H	
162	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$CH_3(CH_2)_4CH(CH_3)$	H	
163	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$(C_2H_5)_2N(CH_2)_3CH(CH_3)$	H	
164	C-Cl	CH	C-CF_3	6-Cl	$(CH_3)_3C$	$CH_2=CHCH_2$	H	
165	C-Cl	CH	C-CF_3	6-Cl	1-methylcyclohexyl	CH_3CH_2	H	
166	C-Cl	CH	CH	5-CF_3	$(CH_3)_3C$	CH_3CH_2	H	

TABLE III (Continued)



Example Number	A	B	W	Yn	R	R3	R16	mp °C
167	C-F	C-F	C-F	5,6-diF	$(CH_3)_3C$	CH_3CH_2	H	
168	C-Br	CH	C-F	6-Br	$(CH_3)_3C$	CH_3CH_2	H	
169	C-Cl	CH	$C-CF_3$	6-Cl	$(CH_3)_3C$		H	

EXAMPLE 170

Insecticidal and Acaricidal Evaluation of N-arylhydazine Derivatives

Test solutions are prepared by dissolving the test compound in a 35% acetone in water mixture to give a concentration of 10,000 ppm. Subsequent dilutions are made with water as needed.

Spodoptera eridania, 3rd instar larvae, southern armyworm

A Sieva limabean leaf expanded to 7-8 cm in length is dipped in the test solution with agitation for 3 seconds and allowed to dry in a hood. The leaf is then placed in a 100 x 10 mm petri dish containing a damp filterpaper on the bottom and ten 3rd instar caterpillars. At 3 and 5 days, observations are made of mortality, reduced feeding, or any interference with normal molting.

Tetranychus urticae(OP-resistant strain), 2-spotted spider mite

Sieva limabean plants with primary leaves expanded to 7-8 cm are selected and cut back to one plant per pot. A small piece is cut from an infested leaf taken from the main colony and placed on each leaf of the test plants. This is done about 2 hours before treatment to allow the mites to move over to the test plant to lay eggs. The size of the cut, infested leaf is varied to obtain about 100 mites per leaf. At the time of test treatment, the piece of leaf used to transfer the mites is removed and discarded. The newly mite-infested plants are dipped in the test solution for 3 seconds with agitation and set in the hood to dry. After 2 days, one leaf is removed and mortality counts are made. After 5 days, another leaf is removed and observations are made of mortality of the eggs and/or newly emerged nymphs.

Diabrotic undecimpunctata howardi, 3rd instar southern corn rootworm

One cc of fine talc is placed in a 30 ml wide-mouth screw-top glass jar. One mL of the appropriate acetone test solution is pipetted onto the talc so as to provide 1.25 mg of active ingredient per jar. The jars are set under a gentle air flow until the acetone is evaporated. The dried talc is loosened, 1 cc of millet seed is added to serve as food for the insects and 25 mL of moist soil is added to each jar. The jar is capped and the contents thoroughly mixed on a Vortex Mixer. Following this, ten 3rd instar rootworms are added to each jar and the jars are loosely capped to allow air exchange for the larvae. The treatments are held for 6 days when mortality counts are made. Missing larvae are presumed dead, since they decompose rapidly and can not be found. The concentrations used in this test correspond approximately to 50 kg/ha.

The tests are rated according to the scale shown below and the data obtained are shown in Tables IV, V and VI.

RATING SCALE			
Rate	% Mortality	Rate	% Mortality
0	no effect	5	56-65
1	10-25	6	66-75
2	26-35	7	76-85
3	36-45	8	86-99
4	46-55	9	100

TABLE IV

Insecticidal and Acaricidal Evaluation of N-Arylamidrazones

Compound (Ex. No.)	% Mortality		
	Armyworm[1] (300 ppm)	2-Spotted Mite[2] (300 ppm)	Corn Rootworm[3] (50 kg/ha)
85	0	0	100
86	100	0	80
87	40	90	100
88	---	---	---
89	0	0	100
90	0	0	20
91	0	80	100
92	0	0	100
93	0	0	100
94	---	80	100
95	80	0	100
96	100	40	80
97	0	0	100
98	40	0	40
100	0	40	0
101	0	0	60
102	0	60	100
103	40	0	100
104	0	90	50
105	20	0	90
106	40	0	100

TABLE IV (Continued)

Compound (Ex. No.)	% Mortality		
	Armyworm[1] (300 ppm)	2-Spotted Mite[2] (300 ppm)	Corn Rootworm[3] (50 kg/ha)
107	---	---	100
108	90	50	100
109	0	0	50
110	0	0	100
111	100	40	90
112	40	100	20
113	20	100	100
114	40	100	100
115	0	0	100
116	20	50	100
117	20	0	100
118	50	70	100
119	100	50	90
120	---	30	20
121	80	40	100
122	0	0	40
123	0	0	60
124	50	80	100
125	0	30	100
126	0	80	90
128	0	0	30
129	100	40	0

TABLE IV (Continued)

Compound (Ex. No.)	% Mortality		
	Armyworm[1] (300 ppm)	2-Spotted Mite[2] (300 ppm)	Corn Rootworm[3] (50 kg/ha)
130	80	80	100
131	70	0	100
132	--	40	100
133	--	0	0
134	0	30	0
135	0	0	0
136	0	70	100
137	0	0	100
138	0	0	100
139	0	70	100
140	0	0	50
141	100	0	0
142	0	0	100
143	0	0	100
144	0	0	100
145	0	0	100
146	0	0	100
147	0	0	100
148	50	0	100
149	100	80	80
150	0	60	100
152	80	0	100

TABLE IV (Continued)

Compound (Ex. No.)	% Mortality		
	Armyworm[1] (300 ppm)	2-Spotted Mite[2] (300 ppm)	Corn Rootworm[3] (50 kg/ha)
153	100	0	100
156	---	0	100
157	0	0	100
158	40	0	100
159	0	0	100
160	0	0	100
161	0	0	---
162	0	100	100
163	0	0	100
164	0	0	100
167	0	0	100
168	0	80	90
169	0	0	100

[1]Armyworm is 3rd instar larvae, southern armyworm

[2]2-Spotted Mite is 2-spotted spider mite (OP-resistant)

[3]Corn Rootworm is 3rd instar southern corn rootworm

TABLE V

Insecticidal and Acaricidal Evaluation of N-Arylhydrazides

Compound (Ex. No.)	Armyworm[1] (300 ppm)	2-Spotted Mite[2] (300 ppm)	Corn Rootworm[3] (50 kg/ha)
1	8	0	9
2	0	0	7
3	---	---	9
4	0	0	7
5	0	0	8
6	0	0	0
7	0	0	0
8	5	0	8
9	0	0	0
10	1	9	3
11	1	0	9
12	4	0	4
13	0	9	3
14	7	0	7
15	9	0	3
16	0	0	0
17	1	3	0
18	2	0	6
19	9	0	0
20	0	0	0
21	0	0	7
22	0	0	0

TABLE V(Continued)

Compound (Ex. No.)	% Mortality Armyworm[1] (300 ppm)	2-Spotted Mite[2] (300 ppm)	Corn Rootworm[3] (50 kg/ha)
23	0	0	0
24	0	0	0
25	9	0	8
26	0	0	0
27	4	0	6
28	2	0	0
29	3	0	0
30	0	2	4
31	0	0	0
32	1	0	0
33	0	0	0
34	8	0	2
35	5	0	0
36	8	0	0
37	4	0	0
39	0	0	0
40	9	0	9
41	3	0	9
42	0	2	4

[1]Armyworm is 3rd instar larvae, southern armyworm
[2]2-Spotted Mite is 2-spotted spider mite (OP-resistant)
[3]Corn Rootworm is 3rd instar southern corn rootworm

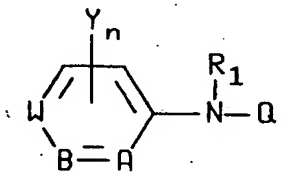
TABLE VI

Insecticidal and Acaricidal Evaluation of Substituted N-Arylhydrazinoyl Halides			
Compound (Ex. No.)	% Mortality		
	Armyworm[1] (300 ppm)	2-Spotted Mite[2] (300 ppm)	Corn Rootworm[3] (50 kg/ha)
78	90	90	0
54	80	100	0
58	0	0	0
59	0	100	0
64	---	90	100
66	80	100	20
71	90	90	30
73	50	100	0
77	100	90	80
79	100	100	100

[1]Armyworm is 3rd instar larvae, southern armyworm
[2]2-Spotted Mite is 2-spotted spider mite (OP-resistant)
[3]Corn Rootworm is 3rd instar southern corn rootworm

Claims

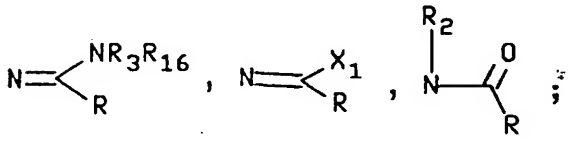
1. A method for the control of insect or acarid pests which comprises contacting said pests or their food supply, habitat or breeding grounds with a pesticidally effective amount of a compound having the structure



(I)

wherein

A is C-R_4 or N;
B is C-R_5 or N;
W is C-R_6 or N with the proviso that at least one of A, B or W must be other than N;
Y is halogen, CN, NO_2, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 alkoxy or C_1-C_6 haloalkoxy;
n is an integer of O, 1 or 2;
Q is



R is hydrogen,

C_1-C_{10}alkyl optionally substituted with one or more halogens, C_3-C_6 cycloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, (C_1-C_4alkyl)SO_x, (C_1-C_4haloalkyl)SO_x, phenyl optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,(C_1-C_4alkyl)SO_x, (C_1-C_4haloalkyl)SO_x, NO_2 or CN groups, or

phenoxy optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,(C_1-C_4alkyl)SO_x, (C_1-C_4haloalkyl)SO_x, NO_2 or CN groups,

C_3-C_{12} cycloalkyl optionally substituted with one or more halogens, C_1-C_6alkyl, C_1-C_6haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, (C_1-C_4alkyl)-SO_x, (C_1-C_4haloalkyl)SO_x,

phenyl optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,NO_2 or CN groups, or

phenoxy optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,NO_2 or CN groups, or

phenyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, NO_2 or CN groups;

R_1 and R_2 are each independently hydrogen or C_1-C_4alkyl;

R_3 and R_{16} are each independently hydrogen,

C_1-C_{10}alkyl optionally substituted with one or more halogen, hydroxy, C_1-C_4alkoxy, (C_1-C_4alkyl)SO_x, $CONR_7R_8$, CO_2R_9, R_{10}, R_{11},

C_3-C_6cycloalkyl optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, NO_2 or CN groups,

phenyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,CO_2 or CN groups, or

pyridyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,NO_2 or CN groups,

C_3-C_{10}alkenyl optionally substituted with one or more halogen, hydroxy, C_1-C_4alkoxy, (C_1-C_4alkyl)SO_x, $CONR_7R_8$, CO_2R_9, R_{10}, R_{11},

C_3-C_6cycloalkyl optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, NO_2 or CN groups,

phenyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,CO_2 or CN groups, or

pyridyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,NO_2 or CN groups,

C_3-C_{10}alkynyl optionally substituted with one or more halogen, hydroxy, C_1-C_4alkoxy, (C_1-C_4alkyl)SO_x, $CONR_7R_8$, CO_2R_9, R_{10}, R_{11},

C_3-C_6cycloalkyl optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, NO_2 or CN groups,

phenyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,CO_2 or CN groups, or

pyridyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,NO_2 or CN groups,

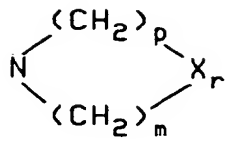
C_3-C_{12}cycloalkyl optionally substituted with one or more halogen, hydroxy, C_1-C_4alkoxy, (C_1-C_4alkyl)SO_x, $CONR_7R_8$, CO_2R_9, R_{10}, R_{11},

C_3-C_6cycloalkyl optionally substituted with one to three halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy, NO_2 or CN groups,

phenyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,CO_2 or CN groups, or

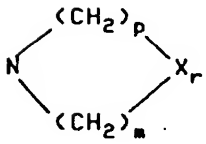
pyridyl optionally substituted with one or more halogen, C_1-C_4alkyl, C_1-C_4haloalkyl, C_1-C_4alkoxy, C_1-C_4haloalkoxy,NO_2 or CN groups or

R_3 and R_{16} may be taken together to form a ring represented by the structure

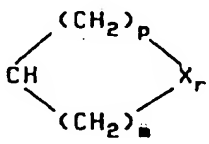


;

R_4, R_5 and R_6	are each independently hydrogen, halogen, CN, NO_2, (C_1-C_4 alkyl)-SO_x,(C_1-C_4 haloalkyl)SO_x, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_1-C_6 alkoxy or C_1-C_6 haloalkoxy;
R_7, R_8 and R_9	are each independently hydrogen or C_1-C_4 alkyl;
R_{10}	is $NR_{12}R_{13}$,

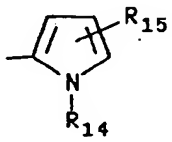


or



;

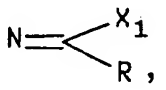
R_{11}	is



;

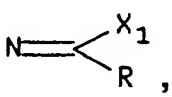
R_{12}, R_{13}, R_{14} and R_{15}	are each independently hydrogen or C_1-C_4 alkyl;
X	is O, S or NR_{14};
X_1	is chlorine, bromine or fluorine;
r	is an integer of 0 or 1;
p and m	are each independently an integer of 0, 1, 2 or 3 with the proviso that only one of p, m or r can be 0 and with the further proviso that the sum of p + m + r must be 4, 5 or 6;
x	is an integer of 0, 1 or 2; or

the acid addition salts thereof with the proviso that when Q is



,

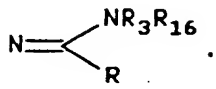
R is C_1-C_5 alkyl and X_1 is chlorine, then either at least one of A, B or W must be N or R_4, R_5, R_6 and Y must be other than hydrogen and n must be O and with the further proviso that when Q is



,

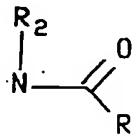
R is phenyl or substituted phenyl and X_1 is chlorine, then at least one of A, B or W must be N.

2. The method according to claim 1 wherein
Q is



3. The method according to claim 2 wherein A is C-R_4, B is CH, W is C-R_6, Y is halogen, n is 1, R_1 is hydrogen, R_4 and R_6 are each independently halogen or C_1-C_6alkyl substituted with one or more halogens, and R, R_3 and R_{16} are each independently hydrogen or C_1-C_{10}alkyl.

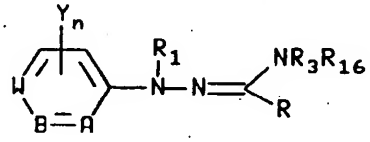
4. The method according to claim 1 wherein Q is



5. The method according to claim 4 wherein R_1 and R_2 are hydrogen, R is C_1-C_6alkyl, A is C-R_3, B is C-R_4, W is C-R_5, Y is halogen, n is 1, R_3 is halogen, R_4 is hydrogen and R_5 is C_1-C_6alkyl substituted with one or more halogens.

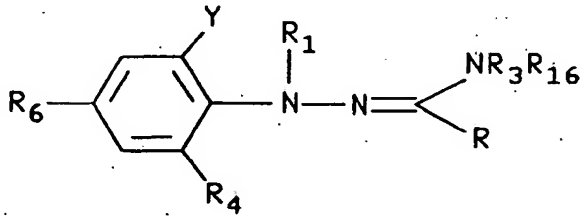
6. The method according to claim 5 wherein the compound is 2,2-dimethylpropionic acid, 2-(2,6-dichloro-α,α,α-trifluoro-p-tolyl)hydrazide.

7. A compound having the structure —



wherein A, B, W, Y, n, R, R_1, R_3 and R_{16} are described in claim 1 with the proviso that when all of A, B and W are other than N, then R and one of R_3 or R_{16} are other than hydrogen and with the further proviso that when one of A, B or W is N, then Y, R_4, R_5 or R_6 must be other than C_1-C_{10}alkyl.

8. The compound according to claim 7 having the structure



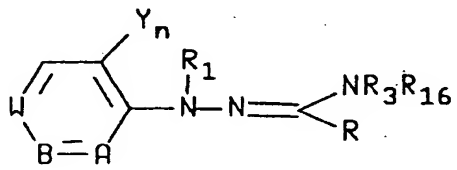
wherein

R	is C_1-C_{10}alkyl;
R_1	is hydrogen or C_1-C_4alkyl;
R_3	is C_1-C_{10}alkyl;
R_{16}	is hydrogen or C_1-C_{10}alkyl; and
R_4, R_6 and Y	are each independently hydrogen, halogen, CN, NO_2, C_1-C_6alkyl, C_1-C_6 haloalkyl,

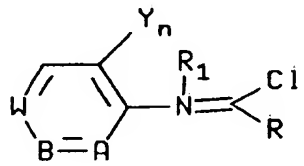
C_1-C_6 alkoxy or C_1-C_6 haloalkoxy.

9. The compound according to claim 8 N-ethyl-2,2- dimethylpropionamide, 2-(2,6-dichloro-α,α,α-trifluoro-p-tolyl)hydrazone

10. A process for the preparation of a compound having the stucture

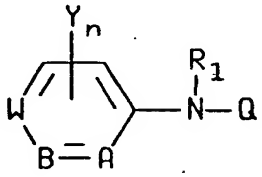


wherein A, B, W, Y, n, R, R_1, R_3 and R_{16} are described in claim 1 which comprises reacting a compound having the structure



with at least one molar equivalent of an amine compound, HNR_3R_{16}.

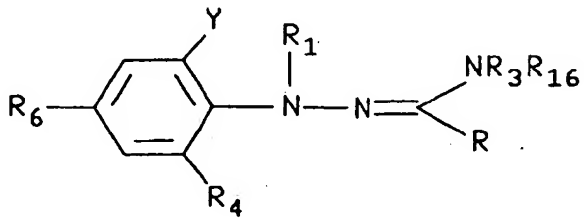
11. A composition for controlling insect or acarid pests which comprises an inert liquid or solid carrier and a pesticidally effective amount of a compound of formula I



(I)

wherein A, B, W, Y, n, R_1 and Q are described in claim 1.

12. The composition according to claim 11 wherein the formula I compound has the structure



and

R	is C_1-C_{10} alkyl;
R_1	is hydrogen or C_1-C_4 alkyl;

R_3	is C_1-C_{10}alkyl;
R_{16}	is hydrogen or C_1-C_{10}alkyl; and
R_4, R_5 and Y	are each independently hydrogen, halogen, CN, NO_2, C_1-C_6alkyl, C_1-C_6 haloalkyl, C_1-C_6alkoxy or C_1-C_6 haloalkoxy.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 9754

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	GB-A-736 473 (BATAAFSCHE PETROLEUM) * claim 1 *	1-3,11, 12	A01N37/28 A01N37/52 A01N43/40 A01N43/58
X	EP-A-0 325 983 (HOECHST) * claims *	1,4,11	C07C257/22
X	US-A-3 745 215 (G. KAUGARS) * column 1, line 30 - line 55 *	1,11	
X	US-A-3 917 849 (R. BOESCH) * claims *	1,11	
X	US-A-3 935 315 (R. BOESCH) * claims *	1,11	
X,P	DE-A-42 00 591 (BAYER) * claims *	1,11	
X	FR-A-2 105 698 (ROUSSEL-UCLAF) * claims 1,3,4 *	7,10,11	
X	US-A-3 214 334 (H.E. FREUND ET AL.) * column 1, line 11 - line 27 *	11	TECHNICAL FIELDS SEARCHED (Int.Cl.5) A01N C07C
X	FR-A-2 184 974 (BAYER) * claims *	11	
A	US-A-3 879 542 (G. KAUGARS) * claims *	1	
X	US-A-3 505 403 (H.G. VIEHE) * claim 6 *	7,8	

-/--

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15 April 1994	Decorte, D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 9754

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	JOURNAL OF ORGANIC CHEMISTRY vol. 38, no. 7 , 1973 , EASTON US pages 1344 - 1348 R.F.SMITH ET AL. 'Amidrazones' *compounds 5,16*	7,8,10	
X	JOURNAL OF THE CHEMICAL SOCIETY, PERKIN TRANSACTIONS 2 1986 , LETCHWORTH GB pages 537 - 541 I.D.CUNNINGHAM ET AL. 'Acid, base, and uncatalysed isomerisation of z- to e-amidine' *page 537, formula 2*	7,8,10	
X	BULLETIN DE LA SOCIETE CHIMIQUE DE FRANCE no. 1 , 1971 , PARIS FR pages 283 - 286 J.P. CHAPELLE ET AL. 'Recherches sur les ènehydrazines' * figure 1 *	7,8	
X	CHEMICAL ABSTRACTS, vol. 92, no. 21, 26 May 1980, Columbus, Ohio, US; abstract no. 180607j, * abstract * & ZH. ORG. KHIM. vol. 15, no. 11 , 1979 pages 2280 - 2287	7,8	TECHNICAL FIELDS SEARCHED (Int.Cl.5)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15 April 1994	Decorte, D

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)